PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-267824

(43)Date of publication of application : 09.10.1998

(51)Int.Cl. G01N 13/00
G01N 1/28
G01N 13/02

(21)Application number : 09-075133

(22)Date of filing : 27.03.1997

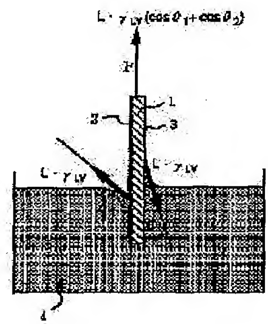
(71)Applicant : AGENCY OF IND SCIENCE & TECHNO

(72)Inventor : TAMADA KAORU
ABE KOJI

(54) METHOD FOR MEASURING DYNAMIC CONTACT ANGLE OF SELF-ORGANIZATION FILM CONTAINING SULFUR ORGANIC MOLECULES

(57)Abstract:

PROBLEM TO BE SOLVED: To measure a contact angle with high accuracy by the Wilhelmy plate method by a method wherein a metal or semiconductor thin film which is formed on one face of a mica substrate is covered with a self-organization monomolecular(SAM) film containing a sulfur organic compound and the mica substrate is then cleaned.



SOLUTION: Preferably, gold is vapor-deposited, to be in a thickness of about 1000 Å, onto one side of a mica substrate 1 which is 1 cm wide, 2 cm high and 50 μm thick, this assembly is immersed in, e.g. the 1 mmol ethanol solution of n- octadecane thiol, and an SAM film 2 such as a fold octadecane thiolate film or the like is formed. The mical substrate 1 is immersed in pure water or the like immediately after a mica exposed face 3 has been cleaned so as to become a clean face, it is displaced at a constant speed, a force F which is applied to a direction perpendicular to the substrate is measured by a microbalance or the like, and the contact angle α1 of the face of the SAM film 2 is computed by a prescribed numerical formula. When the substrate is tilted, a measuring error may be generated. However, when the substrate is loaded with a loa so as to eliminate its inclination, the problem can be solved.

LEGAL STATUS

[Date of request for examination] 27.03.1997

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the

examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]	2972858
[Date of registration]	03.09.1999
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

(19)日本国特許庁（JP）　(12) 公開特許公報（A）　(11)特許出願公開番号

特開平10－267824

(43)公開日　平成10年(1998)10月9日

(51)Int.Cl.6	識別記号	FI	
G01N 13/00		G01N 13/00	
1/28		13/02	
13/02		1/28	N
			G

審査請求　有　請求項の数2　OL　（全 6 頁）

(21)出願番号　特願平9－75133

(22)出願日　平成9年(1997)3月27日

(71)出願人　000001144
工業技術院長
東京都千代田区霞が関1丁目3番1号

(72)発明者　玉田　薫
茨城県つくば市東1丁目1番　工業技術院物質工学工業技術研究所内

(72)発明者　安部　浩司
茨城県つくば市東1丁目1番　工業技術院物質工学工業技術研究所内

(74)指定代理人　工業技術院物質工学工業技術研究所長

(54)【発明の名称】　含硫黄有機分子自己組織化膜の動的接触角の測定方法

(57)【要約】

【課題】　片面だけに含硫黄有機分子SAM膜を有する固体平面基板の接触角をウィルヘルミ・プレート法によって精度良く測定しうる方法を提供する。

【解決手段】　マイカ基板の片面に金属又は半導体の薄膜を形成し、その上に含硫黄有機分子の自己組織化単分子膜を浸漬法又は気化吸着法により被覆し、次いでマイカ基板のマイカ露出面をへき開して、片面が自己組織化単分子膜被覆のマイカ基板を調製し、このマイカ基板の自己組織化単分子膜の動的接触角をウィルヘルミ・プレート法で測定する動的接触角の測定方法。

1　2

【特許請求の範囲】

【請求項１】　マイカ基板の片面に金属又は半導体の薄膜を形成し、その上に含硫黄有機分子の自己組織化単分子膜を浸漬法又は気化吸着法により被覆し、次いでマイカ基板のマイカ露出面をへき開して、片面が自己組織化単分子膜被覆のマイカ基板を調製し、このマイカ基板の自己組織化単分子膜の動的接触角をウィルヘルミ・プレート法で測定することを特徴とする動的接触角の測定方法。

【請求項２】　片面に自己組織化単分子膜被覆を有する前記マイカ基板に、基板が傾かないだけの荷重を付加して測定を行う請求項１記載の動的接触角の測定方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は金属チオラートなどの自己組織化膜の接触角の測定方法に関する。さらに詳しくは、マイカ基板の片面に蒸着した金属又は半導体薄膜上の含硫黄有機分子の単分子膜表面の接触角をウィルヘルミ・プレート法で測定する方法に関する。

【０００２】

【従来の技術】金をはじめとする金属表面に含硫黄有機分子を化学吸着させて作製する単分子膜は、自己組織化膜（Self-Assembled Monolayers, 以下ＳＡＭ膜という）と呼ばれ、近年注目されている。特に金基板とチオール化合物を用いる金チオラートＳＡＭ膜は、金表面を含硫黄有機分子雰囲気下又は希薄溶液中に一定時間放置するだけで、高度に分子配列した単分子膜が得られること、及び金原子とチオール基間の化学反応による吸着により、できた膜の安定性が非常によいことを理由に、現在幅広く研究が進められている。類似する単分子膜技術にラングミュア・ブロジェット法（以下、ＬＢ法という）があるが、ＬＢ法では水面に形成された単分子膜を機械的な手法でガラス固体基板に移し取る（累積操作）のに対し、ＳＡＭ膜では自発的な吸着及び自己組織化プロセスによる固体表面への直接の膜形成のため、膜を移し取るための装置は不要である。また、ＬＢ法では主として分子間の相互作用に基づく分子配列制御が行われるのに対し、ＳＡＭ膜では分子－基板間の相互作用が膜形成プロセスに影響し、例えば基板が金属単結晶の場合、チオール分子が基板の結晶構造に合わせてエピタキシャル成長することが実験的に確認されている（例えば Langmuir 誌、１０巻、２８５３又は３３８３（１９９４年））。ＳＡＭ膜は、接着、耐食、濡れ、トライボロジー（摩擦・潤滑）など、固体表面の処理技術としての利用が期待されるとともに、蛋白質の吸着の際の電極修飾膜、絶縁膜、フォト・電子線・Ｘ線等リソグラフィー技術によるパターニング基板としての利用が検討されている。

【０００３】このような固体表面に吸着した単分子膜の状態を知るための評価法には、接触角法、Ｘ線光電子分光法（ＸＰＳ）、赤外反射吸収法（ＦＴＩＲ－ＲＡＳ）、走査型プローブ顕微鏡での観察などがあるが、中でも接触角法は測定が簡便であり、「濡れ」という実用性に関連の深い情報が得られることから、中心的評価技術として用いられてきている。接触角の測定には、平衡状態で測定する（系を十分に放置し、安定状態に至った状態で測定する）静的測定と、非平衡状態で測定する（系の状態を変えた直後に、あるいは変えながら測定する）動的測定があり、静的測定では表面密度、動的測定では表面の均一性や分子ダイナミクスなどに関する評価が行える。

【０００４】固体平面基板の接触角の測定方法には、大きく分けて、液滴法とつり下げ平板法の２つがある。液滴法は、図２に示したように、水平に置いた固体平面基板５の表面に適当量の液滴６を落とし、基板５と液滴６のなす角度θを直接測定する。一方、つり下げ平板法では、図3に示したように、ビーカー等に入れた液体７中に固体平面基板５を垂直に浸漬し、基板５と液体７のなす角度θを直接測定するか、または基板５に垂直方向に働く力Ｆをミクロ天秤で測定し、この力Ｆと液体の表面張力γ_{LV}及び基板の幅Ｌの関係式（$F=2L\cdot\gamma_{LV}\cdot\cos\theta$）から接触角$\theta$を算出する。つり下げ平板法のうち、後者の接触角を算出する方法はウィルヘルミ・プレート法（Wilhelmy Plate法）と呼ばれている。ウィルヘルミ・プレート法の場合、基板にかかる力を機械的に測定し、その値から接触角を算出するため、目視による読み取り誤差（人的誤差）の生じる他の方法に比べて測定結果の信頼性が高く、誤差も少ない。また、たとえば基板に気－液界面に移動しやすい界面活性物質が含まれている場合、液滴法では基板と液滴の接触面積（液－固界面）に対して液滴の表面積（気－液界面）が同程度であるため、界面活性物質の気－液界面への移動の影響を受けやすいが、つり下げ平板法は液体と基板の接触面積（液－固界面）に比べ液体表面積（気－液界面）がはるかに大きいため、このような影響を受けにくい。さらに、動的測定を行う場合、液滴法では液滴のサイズを変えたり基板を傾けたりしたときの界面移動速度を制御するのが非常に難しいのに対し、つり下げ平板法ではモーター駆動などで基板を引き上げ又は引き下げることにより容易に界面移動速度を制御できる。

【０００５】ところで、従来、例えばガラス上に金薄膜を蒸着する場合、アモルファス金薄膜が形成できるが、両面に均一な膜形成を施すのは難しい。前記の金チオラートＳＡＭ膜形成に用いる金単分子膜の場合は、さらに温度や速度などを制御して行わなければならないため両面に同じ性状の薄膜を形成するのが難しく、また、接触により破壊や汚染も非常に起こりやすいため、表裏を交換して両面に被覆を行うことはさらに困難である。したがって、金チオラートＳＡＭ膜を有する固体基板は、片面だけにＳＡＭ膜を有する非対称基板であり、チオール

吸着のプロセス（溶液浸漬やガス雰囲気下での放置など）においてもう片面は汚染が避けられない。しかし、このような固体基板の接触角は、市販のウィルヘルミ・プレート法を利用した接触角測定装置及び解析ソフトでは測定できなかった。このため従来、金チオラートＳＡＭ膜をはじめとする含硫黄有機分子ＳＡＭ膜の表面性状の接触角による評価は、液滴法による静的測定でのみ行われていた。しかし、前記したように、ウィルヘルミ・プレート法のほうが精度が高いこと、静的測定では表面の不均一性等の評価ができないことなどから、含硫黄有機分子ＳＡＭ膜の接触角をウィルヘルミ・プレート法によって測定する方法の開発が要請されていた。

【０００６】

【発明が解決しようとする課題】したがって本発明は、片面だけに含硫黄有機分子ＳＡＭ膜を有する固体平面基板の接触角をウィルヘルミ・プレート法によって精度良く測定しうる方法を提供することを目的とする。

【０００７】

【課題を解決するための手段】本発明者らは上記課題に鑑み鋭意検討した結果、固体平面基板にマイカ基板を用い、ＳＡＭ膜形成後、接触角測定を行う直前にＳＡＭ膜を有さないマイカ面をへき開することにより、ウィルヘルミ・プレート法で一定の関係式から接触角を導き出すことができることを見出し、この知見に基づき本発明をなすに至った。すなわち本発明は、

（１）マイカ基板の片面に金属又は半導体の薄膜を形成し、その上に含硫黄有機分子の自己組織化単分子膜を浸漬法又は気化吸着法により被覆し、次いでマイカ基板のマイカ露出面をへき開して、片面が自己組織化単分子膜被覆のマイカ基板を調製し、このマイカ基板の自己組織化単分子膜の動的接触角をウィルヘルミ・プレート法で測定することを特徴とする動的接触角の測定方法、及び

（２）片面に自己組織化単分子膜被覆を有する前記マイカ基板に、基板が傾かないだけの荷重を付加して測定を行う（１）項記載の動的接触角の測定方法を提供するものである。

【０００８】

【発明の実施の形態】まず、本発明方法において用いられる測定用マイカ基板の作製法を述べる。本発明で用いるマイカ基板は、接触角測定直前にそのマイカ露出面をへき開して、清浄面にすることができる平面基板であること以外は特に制限はないが、接触角測定時に基板の厚みが基板にかかる力に影響しないよう、厚みが幅の３％以下のものを用いるのが好ましい。また、基板の非対称性のため、測定時に基板に水平方向の力がはたらき、基板を傾斜させて誤差を生むことが考えられるので、この誤差を最小限にする配慮が必要な場合があるが、ＳＡＭ膜作製の基板として通常用いられるサイズ、重量では、このような基板の傾斜、横流しは見られない。また、基板に荷重を付加して基板の傾斜をなくすことにより、この問題は容易に解消することができる。このマイカ基板の片面に、まず金属又は半導体の薄膜を形成する。例えば、マイカ基板上に金単結晶膜を形成する場合、まずマイカへき開面を超高真空チャンバー内（10^{-7}～10^{-9} Ｔｏｒｒ）でプレベイク（マイカへき開面を清浄化するため５００～６００℃の高温で一定時間加熱）した後、温度及び蒸着速度制御下で金を蒸着し、その後再び高温でアニール処理した後、室温に冷却して作製される。蒸着時の基板の最適温度は、通常は３００～４００℃の範囲内であり、蒸着速度及び真空度により多少変動するが、最適温度範囲が狭いので、±５℃程度の微妙な温度制御が必要になる。このため、通常、マイカ基板は基板用ヒーターに背面から均一に接触するようにセットされ、片面のみに金が蒸着される。金単結晶面は接触により破壊や表面汚染がされやすいので、表裏を交換してもう片面にも蒸着するということは通常は行われない。

【０００９】本発明方法における基板上の金属の例としては、前記の金単結晶膜のほかに、銀、銅、白金、水銀、鉄、酸化鉄などがあげられ、特に金が好ましい。また、半導体の例としては、ＧａＡｓ、ＩｎＰなどがあげられる。いずれも通常行われる蒸着等の方法によってマイカ基板上に薄膜を形成することができ、膜厚は通常数１００Å～数１００μｍである。このようにして作製した金属又は半導体薄膜を片面に有するマイカ基板を、含硫黄有機分子雰囲気下に一定時間放置する気化吸着法（蒸着も含む）、含硫黄有機分子希薄溶液中に一定時間浸漬する浸漬法など、通常の自己組織化膜形成の方法、条件で接触角の測定対象であるＳＡＭ膜を形成する。ＳＡＭ膜形成の時間は１ｍｍｏｌの溶液に浸漬した場合、通常数分～２４時間であり、分子鎖長相当の膜厚の単分子膜が得られる。

【００１０】本発明における含硫黄有機分子とは、チオール（－ＳＨ）基、ジスルフィド（－Ｓ－Ｓ－）基、モノスルフィド（－Ｓ－）基、チオフェンなどの含硫黄官能基を有する有機分子であり、チオール基又はジスルフィド基を有する有機分子が好ましく、特にチオール基を有する有機分子が好ましい。有機分子としては例えば、置換基を有してもよい炭素数１～２２、好ましくは４～１８の直鎖又は分岐の脂肪族飽和アルキル、脂肪族不飽和アルキルなどがあげられ、置換基としてはさらに置換されていてもよいフェノキシ基、炭素数１～２２のフルオロアルキル基、カルボン酸基、アミノ基、シアノ基、アミド基、エステル基、スルホン酸基、ハロゲン原子（ブロモ基、クロロ基、ヨード基等）、ピリジン基、ペプチド基、フェロセン基、各種ポリマー鎖、蛋白質や核酸塩基等の生体関連物質などがあげられる。本発明における含硫黄有機分子の具体例としては、例えばオクタデカンチオール、アゾフェノキシドデカンチオール、ペルフルオロオクチルペンタンチオール、ブタンチオール、ヘキサンチオール、オクタンチオール、ドデカンチオー

ル、ジオクタデシルジスルフィド、システイン、シスタミン、チオフェン、メルカプトオクタデシルアミン、メルカプトオクタデカノール、メルカプトオクタデカン酸などがあげられる。

【００１１】次に、本発明方法について図１を参照して説明する。図１は本発明方法の測定原理の説明図であり、従来のつり下げ平板法と同様に、ビーカー等に入れた液体４に片面に含硫黄有機分子ＳＡＭ膜２を有するマイカ基板１を浸漬し、基板１に垂直にかかる力の総和F_{total} をミクロ天秤等の機械的手段で測定する。この力の総和は、下記式（１）で表わされるように、表面張力によって基板１にかかる力（Ｆ）、基板１の重量（ｍｇ）及び浮力（ΔρｇＶ）の和である。

$$F_{total} = F + mg + \Delta\rho gV \qquad (1)$$

ここで、液体４の表面張力によって基板１に垂直方法にかかる力は、含硫黄有機分子ＳＡＭ膜２の表面では下記式（２）で表わされる。

$$F_{SAM} = L \cdot \gamma_{LV} \cdot \cos\theta_1 \qquad (2)$$

（Ｌは基板１の幅、γ_{LV}は液体４の表面張力、θ_1 は金属チオラートＳＡＭ膜２の接触角を表わす。）
また、液体４の表面張力によってＳＡＭ膜を有さないマイカ露出面３に垂直方法にかかる力は下記式（３）で表わされる。

$$F_{mica} = L \cdot \gamma_{LV} \cdot \cos\theta_2 \qquad (3)$$

（θ_2 はマイカ露出面３の接触角を表わす。）よって液体４の表面張力によって基板１に垂直方向にはたらく力Ｆは、下記式（４）で表わされる。

$$F = F_{SAM} + F_{mica} = L \cdot \gamma_{LV} \cdot (\cos\theta_1 + \cos\theta_2) \qquad (4)$$

なお、基板の厚みの影響が実質的に無視でき、上記式（４）が近似的に成立するよう、本発明においては前記したとおりマイカ基板の厚みを幅Ｌの３％以下とするのが好ましい。よって、上記式（１）と式（４）より、へき開したマイカ面の接触角θ_2 、液体４の表面張力γ_{LV}、基板１の幅Ｌをあらかじめ測定しておけば、含硫黄有機分子ＳＡＭ膜２の接触角θ_1 を算出できる。

【００１２】上記のような基板の液体への浸漬、基板にかかる力の測定のための方法や装置は、従来のウィルヘルミ・プレート法について用いることができるものを同様に用いることができる。また、従来のウィルヘルミ・プレート法と同様に、基板をモーター駆動等によって速度制御下で移動することにより、動的接触角の測定ができる。

【００１３】本発明方法において用いることのできる液体は、水、有機溶媒（例えば低級アルコール、ヘキサデカン、デカン、ビシクロヘキシル－１－ブロモナフタレン）などであるが、特に純水を用いた場合はθ_2 が実質的に０であり、上記式（４）は下記の式（５）で表わされる。

$$F = L \cdot \gamma_{LV} \cdot (\cos\theta_1 + 1) \qquad (5)$$

【００１４】
【実施例】次に、本発明を実施例に基づいてさらに詳細に説明する。

【００１５】実施例１
幅１ｃｍ×高さ２ｃｍ×厚さ５０μｍのマイカ基板の片面に、厚さ１０００Åで金を蒸着し、ｎ－オクタデカンチオール（$C_{18}H_{37}SH$）の１ｍｍｏｌエタノール溶液に１時間浸漬して、金オクタデカンチオラートＳＡＭ膜を形成した。このマイカ基板を、マイカ露出面をへき開し清浄面とした直後に純水（イオン交換後、蒸留）に浸漬して一定速度で変位させ、基板に垂直方向にかかる力をミクロ天秤で測定して、前記式（１）及び（５）よりＳＡＭ膜面の接触角を算出した。得られたヒステレシス曲線を図４に示す。図４は横軸を基板の変位（ｍｍ）、縦軸を接触角（°）として測定結果をプロットしたグラフで、グラフ上部が前進方向に変位させたとき、下部が後退方向に変位させたときの結果を示している。測定は前進、後退とも２回行った。この結果、上記の金チオラートＳＡＭ膜の動的接触角として、前進角１１２±１．５°、後退角１００．５±１．５°という値が得られた。前進角は静的測定による接触角とほぼ一致するとされているが、前記の値は静的測定の報告例（例えば Angew. Chem. Int. Ed. Engl.誌、２８巻、５０６（１９８９年）など）の値とほぼ一致した。また、有機シラン系化合物で確認されている多数の測定例において均一かつ高密度に基板に化学吸着したアルキル鎖表面の一般的接触角は、前進角が１１０°前後、後退角が９０～１００°程度という値と比較しても、本実施例の結果は矛盾しない値となっている。また、液滴法で動的接触角を測定した唯一の報告例（Langmuir誌、１０巻、１８２５（１９９４年））において、前進角は１１５°、後退角は１０５°となっており、これと比較しても信頼できる値と考えられる。

【００１６】実施例２
実施例１と同じマイカ基板に実施例１と同様に金を蒸着し、（４－ヘキシルフェニル）アゾフェノキシドデカンチオールの１ｍｍｏｌエタノール溶液に１時間浸漬して、金アゾベンゼンチオラートＳＡＭ膜を形成した。このマイカ基板を、マイカ露出面をへき開し清浄面とした直後に純水に浸漬し、実施例１と同様にして動的接触角

を測定した。測定は前進、後退とも３回行い、実施例１と同様に横軸を変位、縦軸を接触角としてプロットして、図５のヒステレシス曲線を得た。前進角が１０７．５±１°、後退角が９７±１°であった。

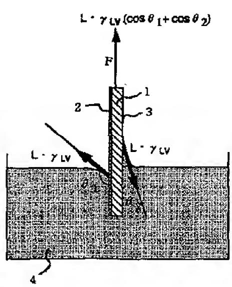
【００１７】実施例３
実施例１と同じマイカ基板に実施例１と同様に金を蒸着し、ペルフルオロオクチルヘキサンチオールの１ｍｍｏｌエタノール溶液に１時間浸漬して、金フルオロアルキルチオラートＳＡＭ膜を形成した。このマイカ基板を、マイカ露出面をへき開し清浄面とした直後に純水に浸漬し、実施例１と同様にして動的接触角を測定した。測定は前進、後退とも３回行い、実施例１と同様に横軸を変位、縦軸を接触角としてプロットして、図６のヒステレシス曲線を得た。前進角が１２０±１°、後退角が１１３±１°であった。この結果は、金フルオロアルキルチオラートＳＡＭ膜の前進角は１１８°との過去の報告（Angew. Chem. Int. Ed. Engl. 誌、２８巻、５０６（１９８９年））ともほぼ一致している。また、ヒステレシスについても、前進角と後退角の差が７°と極めて小さく、化学構造から予想される高密度で安定な化学吸着膜構造と矛盾しない結果が得られた。

【００１８】
【発明の効果】本発明方法によれば、片面のみに含硫黄有機分子ＳＡＭ膜を有するマイカ基板を用いて、含硫黄有機分子ＳＡＭ膜表面の動的接触角の測定を高い精度で行うことができる。本発明では基板にマイカを用いることにより、測定直前のへき開で簡便にマイカ露出面を清浄面とすることができ、金属又は半導体薄膜形成時や含硫黄有機分子ＳＡＭ膜形成時の裏面への汚染の影響を受けることなく接触角の測定が行える。また、マイカへき開面は平滑性が高く、化学的に不活性なので、どのような液体に対しても安定した接触角が得られ、正確な測定が行える。特に基板を純水に浸漬して測定する場合にはマイカ露出面の接触角をゼロとしてＳＡＭ膜の接触角を算出できるため、簡便に精度の高い接触角を得ることができる。

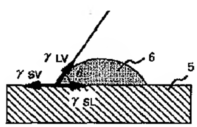
【図面の簡単な説明】
【図１】本発明方法による接触角測定の原理の説明図である。
【図２】液滴法による接触角測定の原理の説明図である。
【図３】つり下げ平板法による接触角測定の原理の説明図である。
【図４】実施例１で測定した動的接触角を、横軸を変位、縦軸を接触角としてプロットしたグラフである。
【図５】実施例２で測定した動的接触角を、横軸を変位、縦軸を接触角としてプロットしたグラフである。
【図６】実施例３で測定した動的接触角を、横軸を変位、縦軸を接触角としてプロットしたグラフである。

【符号の説明】
１　マイカ基板
２　含硫黄有機分子ＳＡＭ膜
３　マイカ露出面
４　液体
５　基板
６　液滴
７　液体

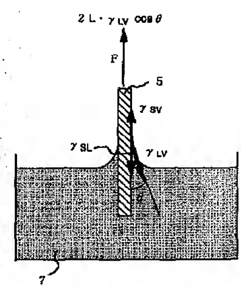
【図１】



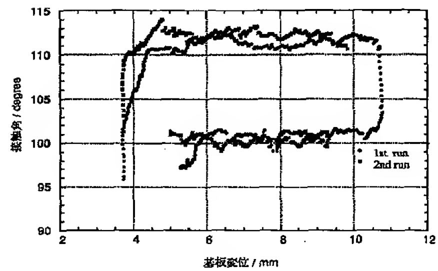
【図２】



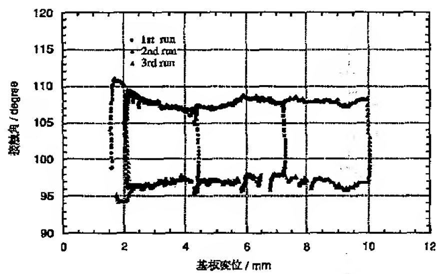
【図３】



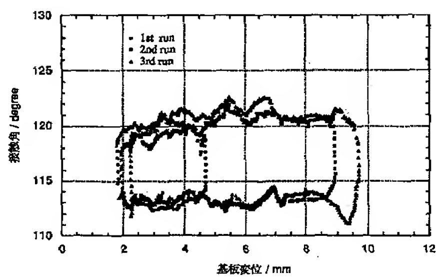
【図４】


115
110
105
100
95
90
2
4
6
8
10
12
接触角 / degree
基板変位 / mm
1st run
2nd run

【図５】


120
115
110
105
100
95
90
0
2
4
6
8
10
12
接触角 / degree
基板変位 / mm
1st run
2nd run
3rd run

【図６】


130
125
120
115
110
0
2
4
6
8
10
12
接触角 / degree
基板変位 / mm
1st run
2nd run
3rd run

* NOTICES *

CLAIMS

[Claim(s)]
[Claim 1] The measuring method of the dynamic contact angle which forms the thin film of a metal or a semiconduc in one side of a mica substrate, covers the self-organizing monomolecular film of a sulfur-containing organic molecu with dip coating or an evaporation adsorption process on it, subsequently carries out the cleavage of the mica expose surface of a mica substrate, and is characterized by for one side preparing the mica substrate of self-organizing monomolecular-film covering, and measuring the dynamic contact angle of the self-organizing monomolecular film this mica substrate by the WIRUHERUMI plate method.
[Claim 2] The measuring method of the dynamic contact angle according to claim 1 which measures by adding only load to which a substrate does not incline to the aforementioned mica substrate which has self-organizing monomolecular-film covering on one side.

[Translation done.]

* NOTICES *

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[The technical field to which invention belongs] this invention relates to the measuring method of the contact angle o self-organizing films, such as metal thio RATO. It is related with the method of measuring in more detail the contact angle on the front face of a monomolecular film of the sulfur-containing organic molecule on the metal deposited on one side of a mica substrate, or a semiconductor thin film by the WIRUHERUMI plate method.
[0002]
[Description of the Prior Art] The monomolecular film which surfaces of metal including gold are made to chemisor sulfur-containing organic molecule, and is produced is called self-organizing film (it is called Self-Assembled Monolayers and a following SAM film), and attracts attention in recent years. Research is broadly advanced now on grounds that the golden thio RATO SAM film especially using a golden substrate and thiol compounds has the very good stability of that the monomolecular film which only carried out fixed time neglect and carried out molecular arrangement of the golden front face highly the bottom of sulfur-containing organic molecule atmosphere or into the dilute solution is obtained and a golden atom, and the film made by adsorption by the chemical reaction between thio groups. Although the Langmuir BUROJIETTO method (henceforth the LB method) is in similar monomolecular-film technology, it receives moving to a glass solid-state substrate by mechanical technique (accumulation operation) in t monomolecular film formed in the water surface by the LB method, and the equipment for moving a film for direct film formation on the front face of a solid-state by spontaneous adsorption and the self-organizing process is unnecessary by the SAM film. Moreover, by the LB method, it is checked experimentally that the interaction betwee molecule-substrates influences a film formation process by the SAM film to molecular arrangement control based on the interaction between molecules mainly being performed, for example, a thiol molecule grows epitaxially accordin to the crystal structure of a substrate when a substrate is a metal single crystal (for example, Langmuir, ten volumes, 2853, or 3383 (1994)). the use a SAM film is [use] as a patterning substrate by lithography technology, such as an electrode ornamentation film in the case of adsorption of protein, an insulator layer, and a photograph, an electron ra an X-ray, while the use as processing technology on front faces of a solid-state, such as adhesion, anticorrosion, wetting, and a tribology (friction - lubricous), is expected is considered
[0003] although the appraisal method for knowing the state of a monomolecular film where it stuck to such a solid-s front face has observation under a contact angle method, X-ray photoelectron spectroscopy (XPS), an infrared reflective absorption process (FTIR-RAS), and a scanned type probe microscope etc. -- inside -- a contact angle meth -- measurement -- simple -- "-- since it gets wet and the deep information on relation is acquired by the practicality " has been used as central evaluation technology Evaluation there are static (system is fully left and it measures in stat where it resulted in stable state) measurement measured by equilibrium, and dynamic (it measures changing immediately after changing state of system) measurement measured by non-equilibrium as measurement of a contact angle, and concerning [concerning surface density by static measurement / measurement] surface homogeneity, surface molecule dynamics, etc. by dynamic measurement can be performed.
[0004] It roughly divides into the measuring method of the contact angle of a solid-state flat-surface substrate, and hangs for it with a sessile drop method, and there are two of plating method in it. As shown in drawing 2 , a sessile drop method drops a suitable quantity of the drop 6 on the front face of the solid-state flat-surface substrate 5 placed horizontally, and measures directly the angle theta which a substrate 5 and a drop 6 make. On the other hand, in lowering plating method, as shown in drawing 3 , the force F which is perpendicularly immersed in the solid-state fla surface substrate 5 into the liquid 7 put into the beaker etc., and measures directly the angle theta which a substrate 5 and a liquid 7 make, or is perpendicularly committed to a substrate 5 is measured by the microbalance, and a contact angle theta is computed from the relational expression (F=2L-gammaLV-costheta) of the width of face L of surface tension gammaLV of this force F and a liquid, and a substrate The method of computing the latter contact angle amo

lowering plating method is called WIRUHERUMI plate method (the Wilhelmy Plate method). In order to measure th force concerning a substrate mechanically in the case of a WIRUHERUMI plate method and to compute a contact angle from the value, compared with other methods which the reading error (human error) by viewing produces, the reliability of a measurement result is high, and there are also few errors. Moreover, compared with the touch area (liquid-******) of a liquid and a substrate, although it is easy to be influenced to the gas-liquid interface of a surface active substance of movement to the touch area (liquid-******) of a substrate and a drop by the sessile drop method since the surface area (gas-liquid interface) of a drop is of the same grade when the surface active substance which is easy to move to a gas-liquid interface is contained in the substrate, for example, since it is far large, as for lowering plating method, a liquid surface area (gas-liquid interface) cannot such be influenced easily Furthermore, when performing dynamic measurement, interface traverse speed can be easily controlled by lowering plating method by raising or reducing a substrate by motorised etc. to one with it very difficult [to control the interface traverse speed when changing the size of a drop or leaning a substrate by the sessile drop method].

[0005] By the way, although an amorphous golden thin film can be formed when carrying out the vacuum evaporatio of the golden thin film on the former, for example, glass, it is difficult to give uniform film formation to both sides. I difficult to form the thin film of the same character as both sides, in order that temperature, speed, etc. may be controlled further in the case of the golden monomolecular film used for the aforementioned golden thio RATO SAM film formation and it may perform them, and since destruction and contamination also tend [very] to take place by contact, it is still more difficult to exchange the front reverse side and to cover to both sides. Therefore, the solid-stat substrate which has a golden thio RATO SAM film is an unsymmetrical substrate which has a SAM film only on on side, and, as for one side, contamination is not avoided any longer in the processes (being solution immersed, neglec under gas atmosphere, etc.) of thiol adsorption. However, the contact angle of such a solid-state substrate has not bee measured with the contact angle measuring device using the commercial WIRUHERUMI plate method, and analysis software. for this reason, the front face of sulfur-containing organic molecule SAM films including a former and gol thio RATO SAM film -- evaluation by the contact angle of a character was performed only by the static measuremen by the sessile drop method However, by that the way of a WIRUHERUMI plate method has a high precision, and sta measurement, as described above, since evaluation of surface heterogeneity etc. was not completed, development of method of measuring the contact angle of a sulfur-containing organic molecule SAM film by the WIRUHERUMI pl method was demanded.

[0006]

[Problem(s) to be Solved by the Invention] Therefore, this invention aims at providing only one side with the method of measuring the contact angle of the solid-state flat-surface substrate which has a sulfur-containing organic molecul SAM film with a sufficient precision by the WIRUHERUMI plate method.

[0007]

[Means for Solving the Problem] As a result of inquiring wholeheartedly in view of the above-mentioned technical problem, by using a mica substrate for a solid-state flat-surface substrate, and carrying out the cleavage of the mica s which does not have a SAM film just before performing contact angle measurement after SAM film formation, this invention persons find out that a contact angle can be drawn from fixed relational expression by the WIRUHERUMI plate method, and came to make this invention based on this knowledge. Namely, this invention forms the thin film o metal or a semiconductor in one side of (1) mica substrate, covers the self-organizing monomolecular film of a sulfu containing organic molecule with dip coating or an evaporation adsorption process on it, and, subsequently carries o the cleavage of the mica exposed surface of a mica substrate. The measuring method of the dynamic contact angle characterized by for one side preparing the mica substrate of self-organizing monomolecular-film covering, and measuring the dynamic contact angle of the self-organizing monomolecular film of this mica substrate by the WIRUHERUMI plate method, And the measuring method of the dynamic contact angle given in (1) term which measures by adding only the load to which a substrate does not incline to the aforementioned mica substrate which h self-organizing monomolecular-film covering on (2) one side is offered.

[0008]

[Embodiments of the Invention] First, the method of producing the mica substrate for measurement used in this invention method is described. Although there is especially no limit except being the flat-surface substrate which the mica substrate used by this invention can carry out the cleavage of the mica exposed surface just before contact angl measurement, and can be made into a pure side, it is desirable that thickness uses 3% or less of thing of width of face that the force which requires the thickness of a substrate for a substrate at the time of contact angle measurement ma not be influenced. Moreover, since it is possible that the force horizontal to a substrate makes ******** and a substr incline at the time of measurement, and an error is induced for the asymmetry of a substrate, although the considerat which makes this error the minimum may be required, by the size and the weight which are usually used as a substra of SAM film production, the inclination of such a substrate and sale through illegal channels are not seen. Moreover

this problem is easily solvable by adding a load to a substrate and losing the inclination of a substrate. The thin film a metal or a semiconductor is first formed in one side of this mica substrate. For example, it is cooled and produced b the room temperature, after carrying out the vacuum evaporationo of the gold under temperature and evaporation-rat control after first carrying out the prebake (it heats fixed time at the elevated temperature of 500-600 degrees C in or to defecate a mica cleavage plane) of the mica cleavage plane within an ultra-high-vacuum chamber (10-7 - 10-9Tor and carrying out annealing processing at an elevated temperature again after that, when forming a golden single crys film on a mica substrate. Although the optimum temperature of the substrate at the time of vacuum evaporationo is usually within the limits of 300-400 degrees C and being somewhat changed with an evaporation rate and a degree o vacuum, since the optimum-temperature range is narrow, an about **5-degree C delicate temperature control is need For this reason, usually, a mica substrate is set so that the heater for substrates may be contacted from a tooth back at homogeneity, and the vacuum evaporationo of the gold is carried out only to one side. As for a golden single crystal side, exchanging the front reverse side, since it is tended to carry out contact destruction and surface contamination, and already carrying out vacuum evaporationo also to one side is not usually performed.

[0009] As an example of the metal on the substrate in this invention method, silver, copper, platinum, mercury, iron, iron oxide, etc. are raised other than the aforementioned golden single crystal film, and especially gold is desirable. Moreover, GaAs, InP, etc. are raised as an example of a semiconductor. Being able to form a thin film on a mica substrate by the methods that all are usually performed, such as vacuum evaporationo, thickness is usually several 100A - 100 micrometers of numbers. Thus, the SAM film which is the measuring object of a contact angle is formed the methods of the usual self-organizing film formation, such as an evaporation adsorption process (vacuum evaporationo is also included) which carries out fixed time neglect of the mica substrate which has the produced met or semiconductor thin film on one side under sulfur-containing organic molecule atmosphere, and dip coating which carries out being fixed time immersed into the sulfur-containing organic molecule dilute solution, and conditions. Th time of SAM film formation is usually several minutes - 24 hours, when it floods with the solution of 1mmol, and th monomolecular film of the thickness of chain length is obtained.

[0010] The organic molecule which the sulfur-containing organic molecule in this invention is an organic molecule which has sulfur-containing functional groups, such as a thiol (-SH) machine, a disulfide (-S-S-) machine, a monosulfide (-S-) machine, and a thiophene, and has a thiol group or a disulfide machine is desirable, and the organi molecule which has especially a thiol group is desirable. the carbon numbers 1-22 which may have a substituent as a organic molecule -- desirable -- the straight chain of 4-18, or the aliphatic saturation alkyl of branching -- The pheno machine which an aliphatic unsaturation alkyl etc. may be raised and may be further replaced as a substituent, The fluoro alkyl group of carbon numbers 1-22, a carboxylic-acid machine, the amino group, a cyano group, Living body related substances, such as an amide group, an ester machine, a sulfonic group, a halogen atom, pyridine machines (a BUROMO machine, a chloro machine, iodine machine, etc.), a peptide machine, a ferrocene machine, various polym chains, protein, and a nucleobase, etc. are raised. As an example of the sulfur-containing organic molecule in this invention, an OKUTA decane thiol, an azo phenoxide decane thiol, a perfluoro-octyl pentanethiol, a butane thiol, a hexane thiol, an octane thiol, a dodecane thiol, dioctadecyl disulfide, a cysteine, cystamine, a thiophene, a mercapto octadecyl amine, a mercapto OKUTA decanol, a mercapto OKUTA decanoic acid, etc. are raised, for example.

[0011] Next, this invention method is explained with reference to drawing 1 . Drawing 1 is the total Ftotal of the forc which is explanatory drawing of the measurement principle of this invention method, is flooded with the liquid 4 put into the beaker etc. like the conventional lowering plating method in the mica substrate 1 which has the sulfur-containing organic molecule SAM film 2 on one side, and is applied at right angles to a substrate 1. It measures by mechanical means, such as microbalance. Total of this force is the weight (mg) of the force (F) applied to a substrate with surface tension, and a substrate 1, and the sum of buoyancy (deltarhogV), as expressed with the following form (1).

Ftotal = F + mg + deltarhogV (1)

Here, the force concerning the perpendicular method is expressed by the following formula (2) to a substrate 1 by the surface tension of a liquid 4 in the front face of the sulfur-containing organic molecule SAM film 2.

FSAM = L-gamma LV-cos theta 1 (2)

((The width of face of a substrate 1 and gammaLV express the surface tension of a liquid 4.) In L, theta 1 expresses t contact angle of the metal thio RATO SAM film 2.)

Moreover, the force concerning the perpendicular method is expressed with the following formula (3) to the mica exposed surface 3 which does not have a SAM film with the surface tension of a liquid 4.

Fmica = L-gamma LV-cos theta 2 (3)

(theta 2 expresses the contact angle of the mica exposed surface 3.) Therefore, perpendicularly, ******** F is expressed by the substrate 1 by the surface tension of a liquid 4 by the following formula (4).

F = FSAM+ Fmica = L-gammaLV- (costheta1 + costheta2) (4)

In addition, it is desirable to make thickness of a mica substrate into 3% or less of the width of face L as it described above in this invention so that the influence of the thickness of a substrate could ignore substantially and the above-mentioned formula (4) might be materialized in approximation. Therefore, if the width of face L of the contact angle theta 2 of the mica side which carried out the cleavage, surface tension gammaLV of a liquid 4, and a substrate 1 is beforehand measured from the above-mentioned formula (1) and the formula (4), it will be the contact angle theta 1 the sulfur-containing organic molecule SAM film 2. It is computable.
[0012] What can be used about the conventional WIRUHERUMI plate method can be similarly used for the method and equipment for measurement of the force concerning being immersed [liquids / of a substrate / above], and a substrate. Moreover, measurement of a dynamic contact angle can be performed by moving a substrate under speed control by motorised etc. like the conventional WIRUHERUMI plate method.
[0013] The liquid which can be used in this invention method is theta 2, when especially pure water is used, although was water, an organic solvent (for example, a lower alcohol, a hexadecane, Deccan, bicyclo hexyl-1-BUROMO naphthalene), etc. It is 0 substantially and the above-mentioned formula (4) is expressed with the following formula

F = L-gammaLV- (costheta1 + 1) (5)
[0014]
[Example] Next, this invention is further explained to a detail based on an example.
[0015] The vacuum evaporationo of the gold was carried out by 1000A in thickness, it flooded with 1mmol ethanol solution of an n octadecane thiol ($C_{18}H_{37}SH$) for 1 hour, and the golden OKUTA decane thio RATO SAM film wa formed in one side of a mica substrate with an one-piece example [1cm] x height [of 2cm] x thickness of 50 micrometers. It was under pure water (distillation after the ion exchange) immediately after carrying out the cleavage the mica exposed surface, and making this mica substrate into a pure side, the variation rate was carried out by const speed, the force perpendicularly applied to a substrate was measured by the microbalance, and the contact angle of a SAM film surface was computed from the aforementioned formula (1) and (5). The obtained hysteresis curve is show in drawing 4 . It is the graph which drawing 4 made the horizontal axis the variation rate (mm) of a substrate, made t vertical axis the contact angle (degree), and plotted the measurement result, and when the graph upper part makes a variation rate carry out in the advance direction, the result when the lower part makes a variation rate carry out in the retreat direction is shown. Advance and retreat performed measurement twice. Consequently, the value of the angula advance of 112**1.5 degrees and the angle of sweepback of 100.5**1.5 degrees was acquired as a dynamic contact angle of the above-mentioned golden thio RATO SAM film. Although angular advance is mostly in agreement with contact angle by static measurement, the aforementioned value carried out simultaneously coincidence with the valu of the examples of a report of static measurement (for example, a Angew.Chem.Int.Ed.Engl. magazine, 28 volumes, 506, etc. (1989)). Moreover, even if angular advance compares with the value of about 90-100 degrees in an angle of sweepback the general contact angle of the alkyl chain front face chemisorbed in the substrate uniformly and with hi density in the example of measurement of a large number currently checked with the organic silane system compoun before and after 110 degrees, the result of this example serves as a value which is not contradictory. Moreover, in the only example of a report (Langmuir, ten volumes, 1825 (1994)) which measured the dynamic contact angle by the sessile drop method, angular advance has become 115 degrees, the angle of sweepback has become 105 degrees, and is considered a value reliable even if it compares with this.
[0016] The vacuum evaporationo of the gold was carried out to the same mica substrate as example 2 example 1 like the example 1, it flooded with 1mmol ethanol solution of an azo (4-hexyl phenyl) phenoxide decane thiol for 1 hour, and the golden azobenzene thio RATO SAM film was formed. It was under pure water immediately after carrying ou the cleavage of the mica exposed surface, and making this mica substrate into a pure side, and the dynamic contact angle was measured like the example 1. Advance and retreat performed measurement 3 times, the variation rate and vertical axis were plotted for the horizontal axis as a contact angle like the example 1, and the hysteresis curve of drawing 5 was obtained. Angular advance was 107.5**1 degree, and the angle of sweepback was 97**1 degree.
[0017] The vacuum evaporationo of the gold was carried out to the same mica substrate as example 3 example 1 like the example 1, it flooded with 1mmol ethanol solution of a perfluoro-octyl hexane thiol for 1 hour, and the golden fluoro alkyl thio RATO SAM film was formed. It was under pure water immediately after carrying out the cleavage the mica exposed surface, and making this mica substrate into a pure side, and the dynamic contact angle was measu like the example 1. Advance and retreat performed measurement 3 times, the variation rate and the vertical axis were plotted for the horizontal axis as a contact angle like the example 1, and the hysteresis curve of drawing 6 was obtain Angular advance was 120**1 degree, and the angle of sweepback was 113**1 degree. In this result, the report (an Angew.Chem.Int.Ed.Engl. magazine, 28 volumes, 506 (1989)) of the 118-degree past is carrying out simultaneously coincidence of the angular advance of a golden fluoro alkyl thio RATO SAM film. Moreover, also about the hystere the difference of angular advance and an angle of sweepback was very as small as 7 degrees, and the result which is

contradictory to the high-density and stable chemisorption membrane structure expected from the chemical structure was obtained.
[0018]
[Effect of the Invention] According to this invention method, the dynamic contact angle of a sulfur-containing organ molecule SAM film front face can be measured in a high precision using the mica substrate which has a sulfur-containing organic molecule SAM film only on one side. In this invention, by using a mica for a substrate, a mica exposed surface can be made into a pure side simple by the cleavage in front of measurement, and a contact angle ca be measured, without being influenced at a metal or the rear face at the time of semiconductor thin film formation an sulfur-containing organic molecule SAM film formation of contamination. Moreover, a mica cleavage plane has high smooth nature, and since it is inactive chemically, the contact angle stabilized to any liquids is obtained, and it can perform exact measurement. Since the contact angle of a SAM film can be computed by making the contact angle of mica exposed surface into zero when it is under pure water and measures especially a substrate, a contact angle with high precision can be obtained simple.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] It is explanatory drawing of the principle of the contact angle measurement by this invention method.
[Drawing 2] It is explanatory drawing of the principle of the contact angle measurement by the sessile drop method.
[Drawing 3] It is explanatory drawing of the principle of the contact angle measurement by lowering plating method
[Drawing 4] It is the graph which plotted [the dynamic contact angle measured in the example 1] the variation rate the vertical axis for the horizontal axis as a contact angle.
[Drawing 5] It is the graph which plotted [the dynamic contact angle measured in the example 2] the variation rate the vertical axis for the horizontal axis as a contact angle.
[Drawing 6] It is the graph which plotted [the dynamic contact angle measured in the example 3] the variation rate the vertical axis for the horizontal axis as a contact angle.
[Description of Notations]
1 Mica Substrate
2 Sulfur-containing Organic Molecule SAM Film
3 Mica Exposed Surface
4 Liquid
5 Substrate
6 Drop
7 Liquid

[Translation done.]

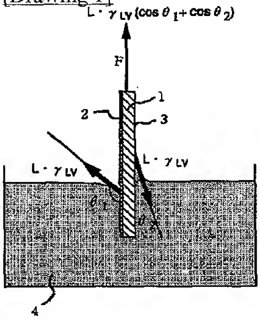
'* NOTICES *

Japan Patent Office is not responsible for any damages caused by the use of this translation.

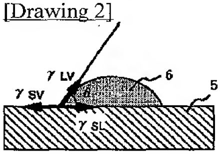
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

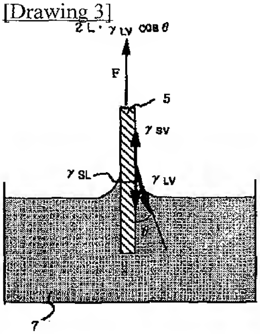
[Drawing 1]



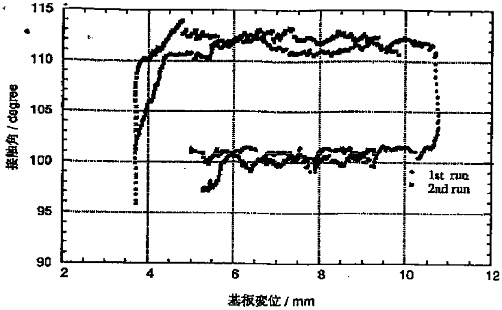
[Drawing 2]



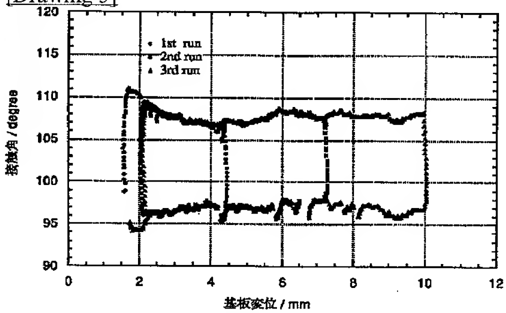
[Drawing 3]



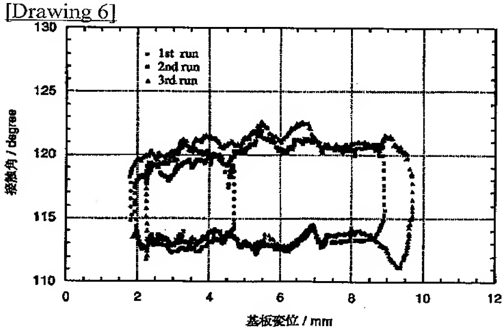
[Drawing 4]



[Drawing 5]



[Drawing 6]



[Translation done.]